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Trivalent Chromium Sorption on Alginate Beads

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The applicability of trivalent chromium removal from aqueous solutions using calcium alginate beads was studied. The equilibrium isotherms were plotted at two temperatures. The relationship between the chromium sorbed and the calcium released was determined as well as the effect of alginate amount and initial pH on the equilibrium results. Chromium sorption kinetics were evaluated as a function of chromium initial concentration and temperature. Transport properties of trivalent chromium on alginate beads were characterised by calculating chromium diffusion coefficients—the Linear Absorption Model and the Shrinking Core Model were assayed. Trivalent chromium removal from aqueous solutions, that made chromium alginate beads by directly dispensing the sodium alginate solution on chromium solutions, was also tested. Finally, a methodology for trivalent chromium removal with alginate is proposed. This method includes two steps: in the first, chromium is removed by using it as an agent for alginate bead formation (for chromium concentrations above 400 mg l^{-1}); afterwards, the obtained solution is placed in contact with previously formed alginate beads for removal of the remaining chromium.

Nomenclature

α	Ratio between the amount of solute in the solution and in the spheres, at equilibrium, dimensionless
a	Parameter of Eq. (8), order of the reaction, dimensionless
C	Concentration of solute in the liquid phase, at equilibrium, mmol l^{-1}
r^2	Correlation coefficient, dimensionless
C^0	Average binding site density, mmol l^{-1} of alginate
C_b	Concentration of free solute inside the sphere, mmol l^{-1} of spheres
$C_{L\infty}$	Concentration of solute in the solution at equilibrium, mmol l^{-1}
C_L,$C_L(t)$	Concentration of solute in the solution, mmol l^{-1}
C_{L0}, C	Initial concentration of solute in the solution, mmol l^{-1}
D_e	Effective diffusion coefficient of the solute in the solid phase, $m^2 s^{-1}$
D_e(LAM)	Diffusion coefficient calculated by LAM, $m^2 s^{-1}$
D_e(SCM)	Diffusion coefficient calculated by SCM, $m^2 s^{-1}$
E_a	Activation energy, J mol^{-1}
F(X)	Function of X, defined by Eq. (7), dimensionless
k	Parameter of Eq. (8), $mol^{1-a} m^{3a-3} s^{-1}$
K	Equilibrium ratio between the concentration of solute immobilised and the concentration of free solute, inside the solid phase, dimensionless
K_p	Partition coefficient of solute between the solid phase (spheres) and the liquid phase, at equilibrium, dimensionless
LAM	Linear absorption model
Mca	Amount of calcium released from the alginate beads at equilibrium, mmol Ca g^{-1} beads
n	Number of alginate beads in the reactor
q	Amount of solute sorbed until equilibrium per unit of mass of adsorbent, mmol g^{-1}
q_n	Positive roots of Eq. (2), dimensionless
r	Radial coordinate of the sphere, m

R	Sphere radius, m
R	Perfect gases constant, $J\,mol^{-1}\,K^{-1}$ (8.314)
r_c	Radius of unchelated core inside the particle, m
SCM	Shrinking core model
t	Time, s (or minutes, if referred), Temperature, K (or °C, if referred)
V	Volume of solution, litre (l)
X, X(t)	Ratio between the amount of solute at solid phase at time t and at equilibrium, defined by Eq. (7), dimensionless

INTRODUCTION

Due to the toxicity and commercial value of heavy metals, it has become increasingly urgent to develop new technologies for its removal from industrial effluents, and its reuse. The conventional physicochemical methods used for this purpose, such as chemical precipitation, electrowinnig, membrane separations, evaporation or resin ionic exchange, can be very expensive, and sometimes not very effective. The biological treatments, based on living microorganisms or plants, could be an alternative method to clean-up industrial wastewaters containing heavy metals. However, these processes are very sensitive to the characteristics of the effluent, as temperature, pH and chemical composition are not suitable for wastewaters with high metal concentrations.

The use of dead biomass and biomass derivatives (biossorbent materials) to remove heavy metals from aqueous solutions, has been widely studied in recent years (Volesky, 1987; Holan *et al.*, 1993; Brady & Tobin, 1994; Kratochvil *et al.*, 1995; etc.). These systems are less expensive than the traditional physicochemical processes. They do not need nutrients and are resistant to the physical-chemical properties of heavy metal solutions.

Alginate, an exopolymer extracted mainly from brown seaweeds, has been used for a long time in several industrial applications. Among recent applications, alginate has been used as a cell immobilisation material (Martinsen *et al.*, 1992) and as a biossorbent material to remove divalent heavy metals, such as Cu^{2+}, Co^{2+}, UO_2^{2+} and Zn^{2+} from aqueous solutions. Alginate showed good metal sorption efficiency (Jang *et al.*, 1991; Apel & Torma, 1993; Chen *et al.*, 1993; Lewandowski & Roe, 1994).

Alginates are salts of unbranched copolymers, with 1→4 links, of β-D-mannuronic and α-L-guluronic acids (Smidsrød & Skjåk-Brœk, 1990). They produce thermally irreversible gels by association with most divalent cations.

Trivalent chromium is widely used in tanning industries and electrodeposition processes that generate high volumes of effluents at high chromium concentrations. Although trivalent chromium is not particularly toxic, its disposal as liquid effluents in natural waters or as sludges in soils, has to be avoided and controlled, for it may be oxidized, especially in soils, to the hexavalent form, which is highly toxic an carcinogenic.

The aim of this work is to develop a method to remove trivalent chromium from liquid effluents using alginate beads as sorption material. Characterisation of sorption mechanisms as well as transport properties will be studied.

MATERIALS AND METHODS

Chemicals

Sodium alginate (Manutex, RSX, Kelco Co.) was purchased from Sarcol Porto, Portugal). All the other chemicals were analytical grade.

Experimental

Bead preparation

Calcium alginate beads were prepared by dropping a 3% (w/v) sodium alginate aqueous solution on a stirred 2% (w/v) calcium chloride solution. The beads were stirred in the $CaCl_2$ solution for 24 hours. They were then washed three times with distilled water and maintained in a 2% $CaCl_2$ solution at 4°C.

Immediately before use, the calcium alginate beads were washed again three times with distilled water and the excess water was absorbed on filter paper.

The mean diameter (2.58 mm) of beads was determined in a sample of 50 alginate beads using a micrometer. The mean weight (9.30 mg) of the beads was determined using 50 samples of 20 beads. The percentage of alginate on the beads [5.6% (w/v)] was calculated making a material balance, after measuring the volume of beads obtained from a defined volume of sodium alginate solution. The solids content of the alginate beads [6.2% (w/w)] was obtained by drying at 105°C until constant weight.

Equilibrium experiments

Solutions of $Cr(NO_3)_3$ in 0.01 M aqueous solution of $NaNO_3$ with chromium concentrations varying from 0.0001 M to 0.08 M were prepared in volumetric flasks. Aliquots of 100 ml of these solutions were transferred to 250 ml screw-capped polyethylene Erlenmeyer's flasks. The pH of the solutions was measured.

Aliquots (9.30 g) of calcium alginate beads (1000±3 beads) were weighed and added to the chromium (III) solutions to obtain 10 beads per ml of chromium solution.

The flasks were closed and shaked on the orbital shaker at 200 rpm and at temperatures between 10 and 27°C.

The experiments were concluded after 8 hours: it was experimentally determined that at the end of this period equilibrium had been achieved. Final pH was measured (at the temperature of 27°C).

Samples of the treated solution were removed, diluted, acidified with HNO_3 to a pH of below 2, and kept at 4°C for subsequent analysis. Chromium was determined by atomic absorption spectroscopy and calcium by flame emission spectroscopy.

Kinetics experiments

Solutions of $Cr(NO_3)_3$ in 0.01 M $NaNO_3$ aqueous solution with chromium (III) concentrations from 0.0001 M (5.2 mg $Cr\,l^{-1}$) to 0.02 M (1040 mg $Cr\,l^{-1}$) were prepared in volumetric flasks. Aliquots of 250 Ml of these solutions were transferred to 500-ml screw-capped polyethylene Erlenmeyer's flasks.

Aliquots (23.25 g) of calcium alginate beads (2500±10 beads) were weighed, to obtain 10 beads per ml of chromium solution (corresponding to 5.2 g l^{-1} dry alginate). The flasks and the alginate beads (separately) were placed inside an incubator to achieve the desired temperature. After thermal equilibrium, the alginate beads were added to the chromium (III) solutions, the flasks were closed and placed immediately on the orbital shaker-incubator set at 200 rpm at the desired temperature.

At appropriate time periods, 1 ml samples were removed, acidified with HNO_3 to pH below 2, diluted and kept at 4°C. They were subsequently analysed by atomic absorption spectroscopy for chromium.

Mathematical models

To calculate the diffusion coefficients of trivalent chromium in the alginate beads, two models were used: the linear absorption model, LAM, and the shrinking core model, SCM.

It is assumed that sorption occurs from a well-stirred solution of initial solute concentration C_{L0} and finite volume V, into a spherical particle initially without solute. In both models it is assumed that there is chemical reaction of the solute with active sites inside the sphere, but the reaction rate is much higher than the rate of diffusion in the particle, and also that there is no resistance to mass transfer in the film around the sphere. In other words, the diffusion of the solute inside the particle is considered the limiting step of the sorption process.

Figure 1 represents a scheme of the concentration profiles inside a spherical particle, according to both models cited.

LINEAR ABSORPTION MODEL (LAM)

The LAM, based on Fick's law and presented by Crank (1956), assumes that at each point inside the sphere there is a local equilibrium between the reacted and the free solute, and, for this case the equation representing the concentration in solution as a function of time is:

$$C_L(t) = \frac{\alpha C_{L0}}{1+\alpha} = 6\alpha C_{L0} \sum_{n=1}^{\infty} \frac{\exp[-D_e q_n^2 t/(R^2 K_p)]}{9 + 9\alpha + q_n^2 \alpha^2} \tag{1}$$

where q_n are the positive roots of the equation:

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \tag{2}$$

α is defined by:

$$\alpha = \frac{C_{L\infty}}{C_{L0} - C_{L\infty}} \tag{3}$$

where K_p is the partition coefficient between the solid and liquid phase, equal to (K + 1), and K the equilibrium ratio between the immobilised and the diffusing substance.

SHRINKING CORE MODEL (SCM)

The SCM, applied by Levenspiel (1972) to fluid particle chemical reactions, and more specifically to ionic exchange of heavy metals by Rao & Gupta (1982), assumes that the diffusion through a reacted shell is the limiting step, and that an

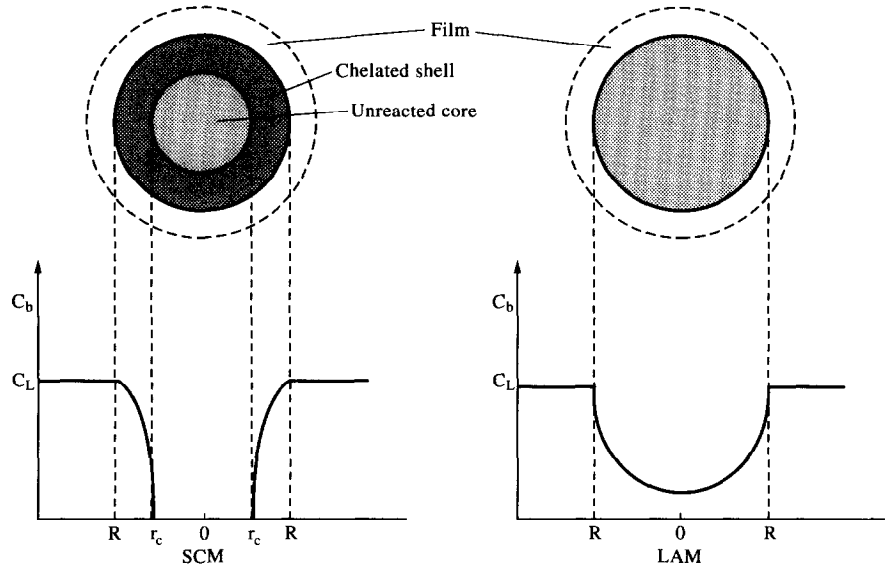

Fig. 1. Scheme of the concentration profile inside a sphere, according to both models, SCM and LAM, considering the diffusion in the sphere of the limiting step (adapted from Levenspiel, 1972).

unreacted core is shrinking as time proceeds. The final equation is:

$$[1 - 3(1 - X)^{2/3} + 2(1 - X)] = \frac{6D_e}{c^0R^2}\int_0^t C_L dt \quad (4)$$

Calling F(X) to the function:

$$F(X) = [1 - 3(1 - X)^{2/3} + 2(1 - X)] \quad (5)$$

then a plot of F(X) versus $\int_0^t C_L dt$ will give a straight fine of slope $(6D_e)/(C^0R^2)$, where the diffusion coefficient of the metal on the particle can be obtained.

Jang *et al.* (1991 and Jang, 1994), Chen *et al.* (1993), and Lewandowski & Roe (1994), applied this model to calculate the diffusion coefficient of copper (Cu^{2+}) on calcium alginate beads, having considered C^0 as the average binding site density of the spheres, defined by:

$$C^0 = \frac{(C_{L0} - C_{L\infty})V}{n\frac{4}{3}\pi R^3} \quad (6)$$

and calculated X from the equation:

$$X(t) = \frac{[C_{L0} - C_L(t)]}{[C_{L0} - C_{L\infty}]} \quad (7)$$

RESULTS AND DISCUSSION

Equilibrium results

Equilibrium isotherms

The relationship obtained between chromium concentrations in the alginate beads and in the solution at equilibrium (isotherms), is shown in Fig. 2 for two temperatures. According to Brunauer classification (Figueiredo, 1981), the isotherms are of type IV, for they have an inflexion point and a maximum concentration on the beads.

Figure 2 shows that at the temperature of 27°C, the capacity of the alginate beads to remove chromium is higher than at 10°C. The difference increases as the concentration on the beads reaches the saturation value. At 27°C, the saturation concentration of the beads at 27°C is 0.15 mmol chromium g^{-1}, which is a value 50% higher than saturation concentration at 10°C (0.10 mmol chromium g^{-1}).

Furthermore, the isotherms at 27°C show an inflexion point at chromium concentrations on the solution of about 10 mmol l^{-1}, and chromium concentrations on the beads of 0.065 mmol g^{-1} (3.4 mg g^{-1}) and at 10°C of 0.055 mmol g^{-1} (2.9 mg g^{-1}). These inflexion points indicate that there are at least two different mechanisms of chromium sorption.

Figure 3 shows the amount of calcium released from the alginate beads MCa (expressed in mmol Ca g^{-1} beads) as a function of the amount of chromium sorbed. This plot confirms that there is more than one mechanism of sorption.

At chromium concentrations below the inflexion point on the isotherms (~0.06 mmol g^{-1}), the chromium sorbed is accompanied by calcium release, with a ratio of 1.3 mol Ca^{2+} mol^{-1} Cr^{3+}.

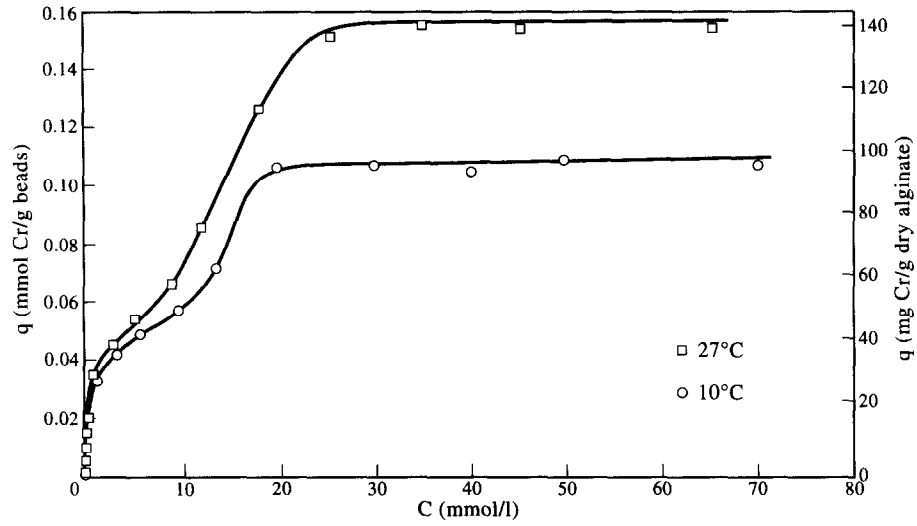

Fig. 2. Equilibrium isotherms: chromium concentration in the beads (q) as a function of chromium concentration in the solution (C), at equilibrium, at two temperatures, using 5.2 g dry alginate/litre of solution (93 g beads/l).

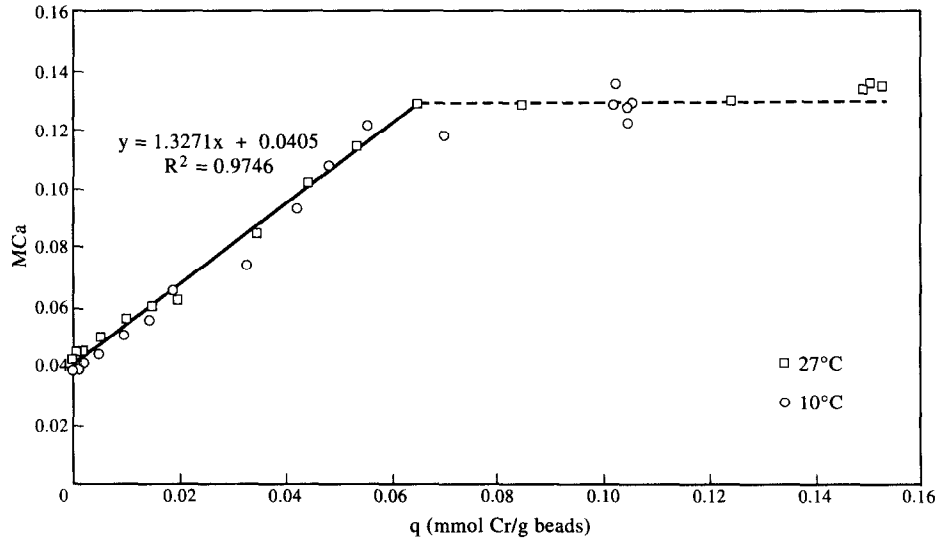

Fig. 3. Amount of calcium released from the alginate beads as a function of the amount of chromium sorbed, at equilibrium.

This slope lies between the stoichiometric ratio for Ca^{2+}/Cr^{3+} (1.5) and $Ca^{2+}/CrOH^{2+}$. Since at the working pH range (2.5–4), both of these species (Cr^{3+} and $CrOH^{2+}$) coexist in equilibrium (Leyva-Ramos *et al.*, 1995), we can then postulate that at low and medium chromium concentrations (below 10 mmol Cr(III)/l^{-1}), the ionic exchange is the predominant sorption mechanism. For higher concentrations of chromium, other mechanisms of sorption occur, for there is no further release of calcium as the amount of chromium sorbed by the alginate increases.

The maximum chromium sorption achieved by the alginate beads was 0.14 g Cr g^{-1} dry alginate at 27°C and 0.10 g Cr g^{-1} dry alginate at 10°C. In comparison, Jang *et al.*, 1991, obtained for copper sorption, a value of 0.09 g Cu g^{-1} dry alginate.

EFFECT OF ALGINATE AMOUNT ON EQUILIBRIUM RESULTS

The relations between the amount of alginate beads (expressed as beads dry weight) and the chromium removal $[(C_{L\infty}-C_{L0})/C_{L0}]$, was studied at two initial chromium concentrations (8 and 20 mmol l^{-1} at 10°C. The results are presented in Fig. 4. Although a more efficient removal is obtained for higher alginate concentrations, as expected, results suggest the existence of transport limitations when more alginate is used.

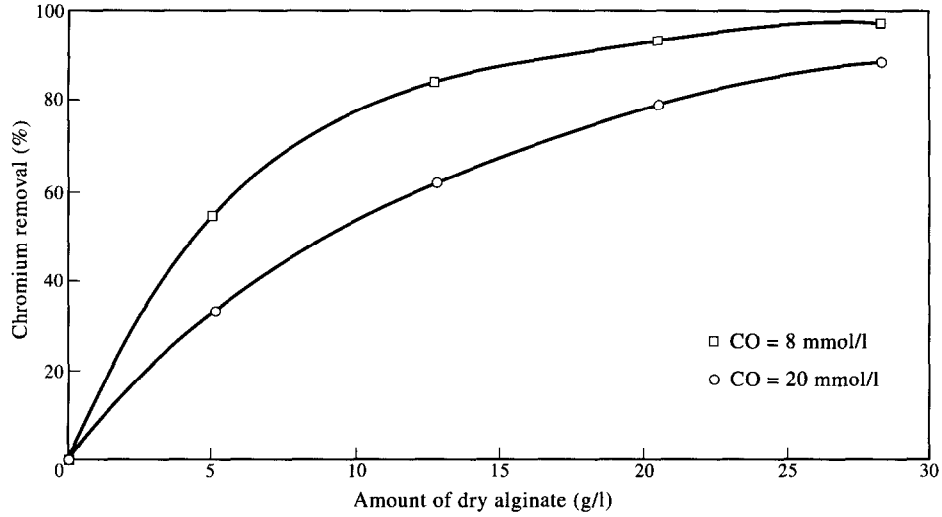

Fig. 4. Efficiency of chromium removal by the calcium alginate beads, as a function of amount of dry alginate for two initial chromium concentrations.

EFFECT OF PH ON EQUILIBRIUM RESULTS

Figure 5 represents the chromium sorption by the alginate beads at different initial pH values for 0.02 M $Cr(NO_3)_3$ solutions. As the plot shows, in the range studied (pH 2–4), higher pH values resulted in higher chromium sorption.

According to the speciation diagram for Cr(III) complexes in aqueous solutions, from Leyva-Ramos *et al.* (1995), at pH 2 the molar percentage of Cr^{3+} is 98% of the total amount of chromium in solution, while at pH 4, this value decreases to about 40% and almost 60% is in the ionic form $CrOH^{2+}$ (and a trace amount of $Cr(OH)_4{}^{5+}$).

The stoichiometric relationship for the ionic exchange between calcium and chromium occurring on the alginate beads, is of 1.5:1 for Ca^{2+} to Cr^{3+}, and 1:1 for Ca^{2+} to $CrOH^{2+}$. To a specific amount of Ca^{2+} ions available to ionic exchange in the alginate, the same amount of $CrOH^{2+}$ ions can be removed, while only 67% (1/1.5) of that amount of Cr^{3+} ions can be exchanged. This is probably the major reason, because at pH 4 where about 60% of the chromium is in the ionic form of $CrOH^{2+}$, the chromium sorption is higher than at pH 2, where almost all the chromium is in the ionic form Cr^{3+}. However, theoretically, at pH 4, the chromium removal should have increased by 15%. The experimental increase was 23%, which suggests that some other factors might account for this difference. For example, alginate might have different affinities to the different species of chromium existing in the solution, or its affinity towards chromate might be affected by its interactions with other ions. Also, at lower pH, there is a smaller amount of carboxylic groups available for gel formation and consequently the ionic exchange process might be reduced.

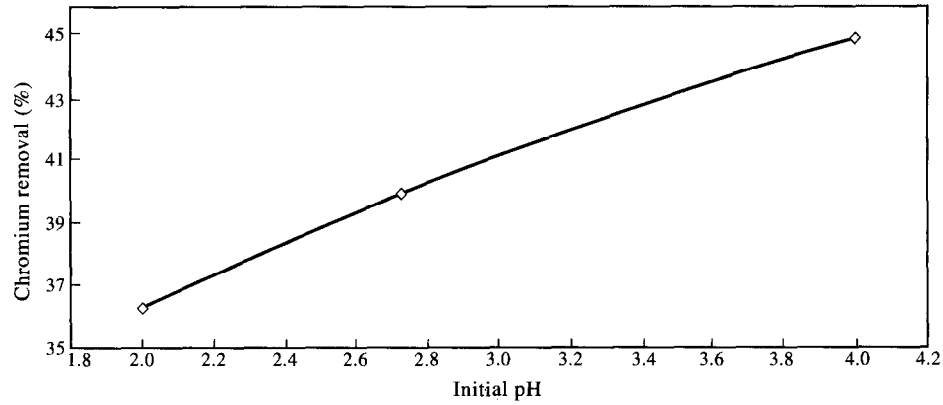

Fig. 5. Effect of initial pH on chromium removal by the calcium alginate beads, for an initial concentration of 20 mmol/l, at 27°C.

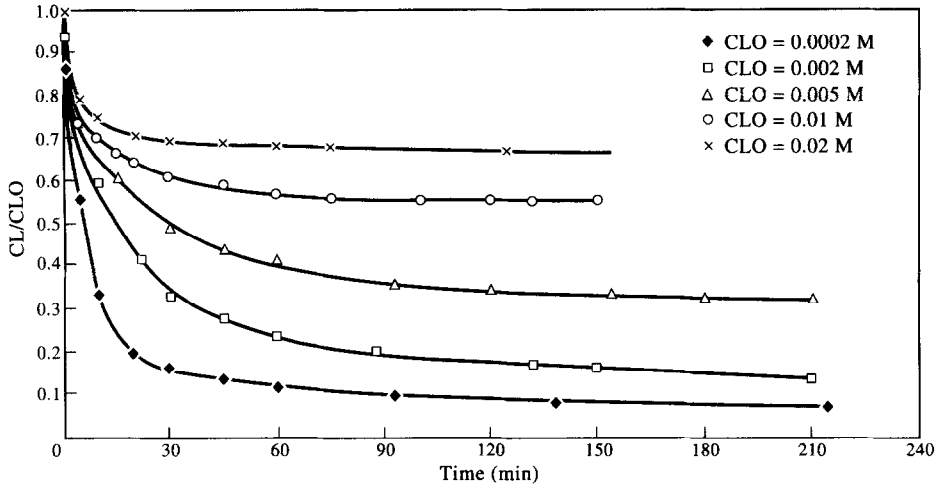

Fig. 6. Normalised chromium concentration (C_L/C_{L0}) as a function of time, at different initial chromium concentrations (C_{L0}), at 10°C, using 5.2 g dry alginate per litre of chromium solution.

Kinetics experiments

Some of the experiments made at different initial chromium concentrations (C_{L0}) are represented in Fig. 6. This figure shows the normalised concentration (C_L/C_{L0}) as a function of time at 10°C.

Using these and other experiments, an attempt was made to fit the sorption rate Eq. (8) to the experimental results:

$$-dC_L/dt = kC_L^a \quad (8)$$

where $-dC_L/dt$ is the rate of chromium sorption by the alginate beads, a is the reaction order relative to chromium concentration, and k is the rate constant (Levenspiel, 1972). Since the alginate concentration was the same in all experiments, these parameters were calculated by the initial rate method (during the first 5 minutes $\{-dC_L/dt = [C_{L0} - C_{L0} = 5\,\text{min})]/(5\times60)\}$). These results are plotted in Fig. 7.

The rate equation then obtained, with respect to chromium concentration on the solution (C_L) was:

$$-dC_L/dt[\text{mmol}\,l^{-1}s^{-1})] = 0.00115C_L^{0.84}$$

Determination of diffusion coefficients

The diffusion coefficients were calculated by the LAM and SCM models (briefly described on the section Materials and methods) and are plotted in Fig. 8, as a function of initial chromium concentration at 10°C.

To calculate D_e(LAM), the best fit to Eq. (1)

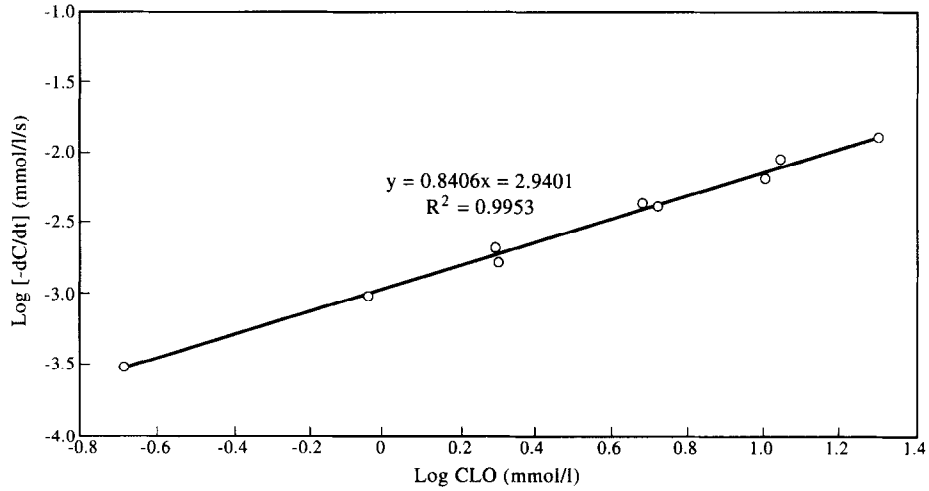

Fig. 7. Logarithm of the initial rate of chromium sorption as a function of the logarithm of initial chromium concentration in solution, at 10°C, using 5.2 g dry alginate per litre of chromium solution.

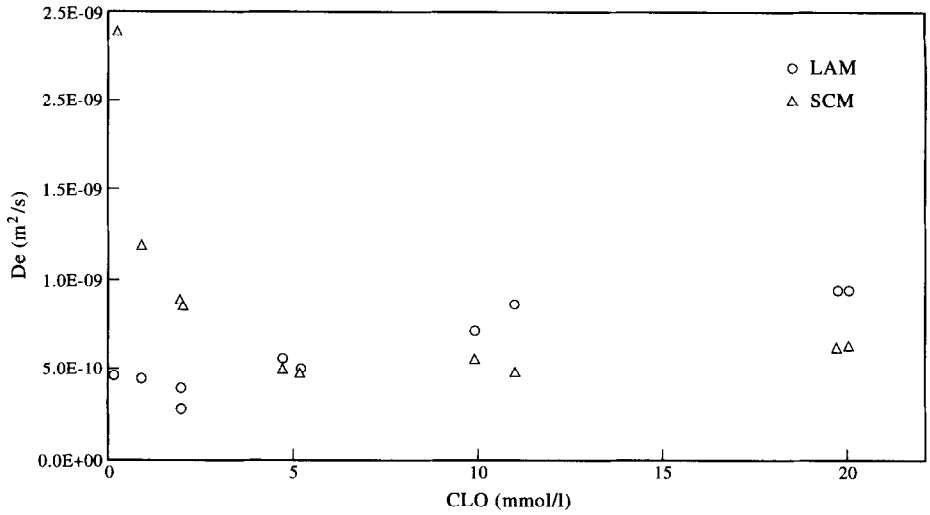

Fig. 8. Diffusion coefficients of chromium in alginate beads, as a function of the initial chromium concentration in solution, calculated by the two different models (LAM and SCM). The experiment was set at 10°C, with 10 alginate beads/ml (5.2 g dry alginate per litre of chromium solution).

was determined, having the number of terms of the sum been limited to 200.

To calculate D_e(SCM), a plot of F(X) versus $\int_0^t C_L dt$ was made. For the lower values of $\int_0^t C_L dt$ the results were fitted to a straight line, and by multiplying the corresponding slope by (C_{L0}*R^2/6), D_e(SCM) is obtained. The values of $\int_0^t C_L dt$were calculated by integration of $C_L(t)$ by the trapezoid rule.

The analysis of the correlation coefficients obtained after fitting the experimental data to LAM and SCM models allowed us to conclude that LAM describes better the diffusion process for larger chromium concentrations, while for the smaller concentrations SCM is the best model. This can be explained by the fact that at low concentration the ionic exchange is the governing mechanism, while at higher concentration this mechanism does not prevail.

Figure 8 presents a plot of the diffusion coefficients calculated by the two models, LAM and SCM, as a function of initial chromium concentration in the solution at 10°C. The analysis of this figure indicates that:

diffusion coefficients obtained by SCM model are much more dependent on chromium concentration than those obtained by LAM model

at low chromium concentration (below 2 mmol l^{-1}), D_e(LAM) and D_e(SCM) are quite different, with D_e(SCM) being superior to D_e(LAM). In this region, D_e(SCM) decreases almost exponentially with the increase of chromium concentration (from 2.39×10^{-9} m^2s^{-1} for C_{L0} = 0.2 mmol l^{-1} until 5.01×10^{-10} m^2s^{-1} for C_{L0} = 2 mmol l^{-1}), while D_e(LAM) just reduces slightly (from 4.70×10^{-10} m^2s^{-1} for C_{L0} = 0.2 mmol l^{-1} until about 3×10^{-10} m^2s^{-1} for C_{L0} = 2 mmol l^{-1}).

at higher chromium concentration (above 10 mmol l^{-1}), D_e(SCM) is inferior to D_e(LAM), but the difference does not seem to increase as the chromium concentration becomes larger.

the results obtained for D_e(SCM) and D_e(LAM) are not very different in the region of initial chromium concentration of about 5 mmol l^{-1}.

Jang *et al.* (1991) applied the SCM to diffusion of Cu^{2+} in alginate gels, having concluded that this model describes satisfactorily the process, except for periods toward the end of absorption.Chen *et al.* (1993) applied both models, LAM and SCM, to the diffusion of Cu^{2+} in calcium alginate beads, having concluded that LAM is preferable to the SCM for this system, because with LAM a dependence of the diffusion coefficient on alginate concentration on the beads was obtained. Using the data of Chen *et al.* (1993) a recalculation of the diffusion coefficients was made by Lewandowski & Roe (1994). It was confirmed that the diffusivity increases with increasing alginate concentration, but at a lower rate than reported by Chen *et al.* (1993). For experiments with initial concentration of 1 mmol l^{-1} $CuCl_2$, at 25°C, the diffusivity of Cu^{2+} in alginate beads (with 3% of alginate) was 0.98×10^{-9} m^2s^{-1}, for the SCM, and 1.08×10^{-9} m^2s^{-1} for LAM.In all our experiments,

a constant alginate concentration (3%) in the beads, was used for different initial chromium concentrations. The temperature was 10°C, and the anion used was nitrate. This was used because of problems arising from the use of chloride, since this anion forms complexes with chromium. The calculated diffusion coefficients for the experiment (chromium initial concentration of 0.90 mmol l^{-1}) presenting the closest experimental conditions to those of Chen *et al.* (1993) were 1.20×10^{-9} m^2s^{-1} (SCM) and 4.51×10^{-10} m^2s^{-1} (LAM). Although, it is not adequate to compare values with different experimental conditions, it may be seen that they are of the same order of magnitude of those obtained for copper ions. The variation of chromium diffusion coefficients with chromium concentration may be explained, as Tyrrel & Harris (1984) pointed out, by the fact that the diffusion coefficients of electrolytes change with concentration in ways that are difficult to predict. In their work involving aqueous halides, as concentration increased, there was an initial rapid fall on diffusion coefficients leading to a minimum value, followed by an increase. This is the type of behaviour obtained in this work for D_e(SCM).

EFFECT OF TEMPERATURE

The influence of temperature was studied for the initial concentration of 20 mmol l^{-1} chromium, using 5.2 g dry alginate l^{-1} (10 beads per ml). The results obtained are shown in Fig. 9.

Figure 10 presents the Arrhenius plot for chromium diffusion coefficients determined by LAM and SCM models. The activation energy of the diffusion process (E_a), was obtained considering D_e proportional to $e^{-Ea/(RT)}$. The values obtained were 32.9 kJ mol^{-1}, using D_e(LAM), and 52.1 kJ mol^{-1}, using D_e(SCM). Using the SCM, the fit to Arrhenius equation was much better.

Chromium removal by manufacture of chromium alginate beads

The removal of chromium from concentrated solutions of $Cr(NO_3)_3$ by dropping the sodium alginate solution directly on the chromium solution, was studied. Figure 11 represents the chromium concentration in a stirred solution as a function of the amount of sodium alginate solution added.

It was verified that this method is applicable for chromium concentration above 400 mg $Cr l^{-1}$. At lower concentrations, there is no significant formation of beads.

During this experiment, the pH of the solution changed from an initial value of 2.95 to 3.45 when chromium concentration on the solution was 400 mg l^{-1}. At pH 2.95, approximately 90% of chromium is in the trivalent form while at pH 3.45 the proportion of trivalent chromium is 75%, the remaining being present as $CrOH^{2+}$. This indicates that the main mechanism for chromium alginate gel formation involves the interaction between the carboxylic groups of alginic acid and the trivalent form of the chromium ion, since this is the ionic form that predominates during all the experiment.

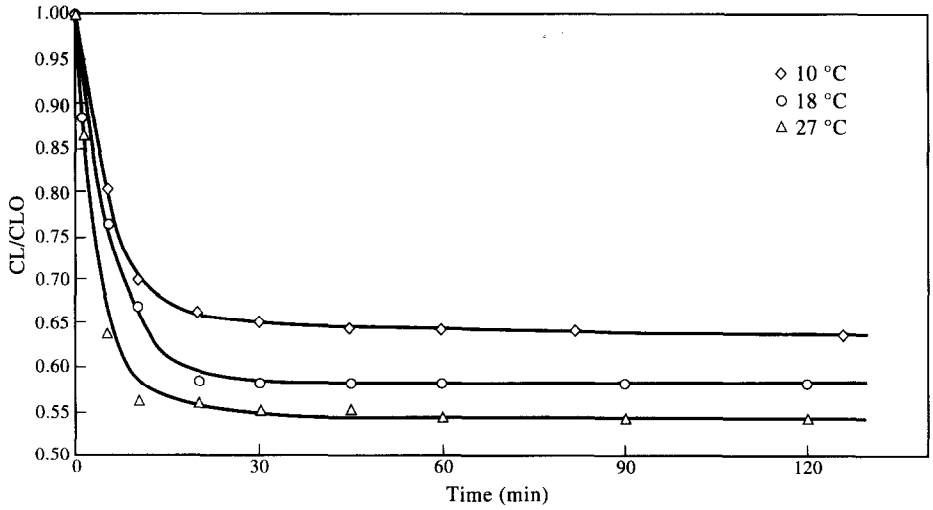

Fig. 9. Normalised chromium concentration (C_L/C_{L0}) as a function of time, at different temperatures, for 20 mmol/l initial chromium concentration (C_{L0}), using 5.2 g dry alginate per litre of chromium solution.

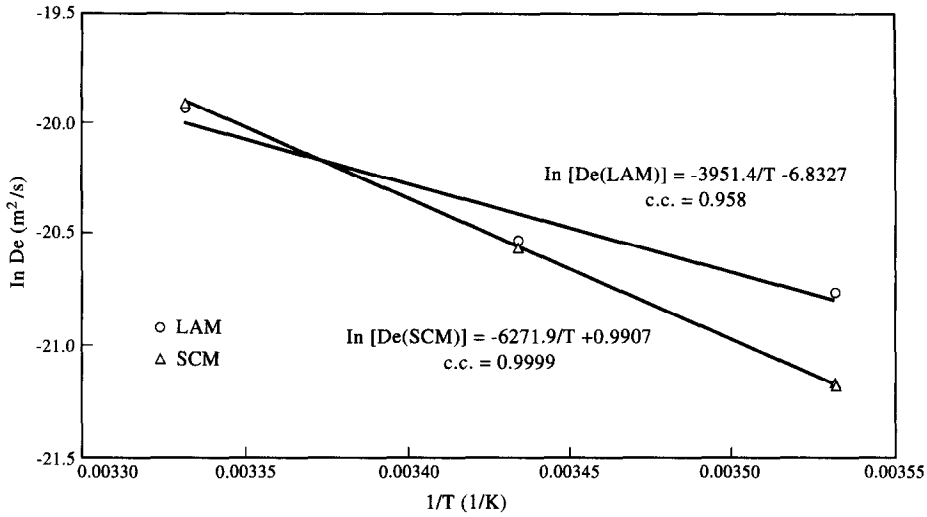

Fig. 10. Arrhenius plots, obtained using the diffusion coefficients calculated by the two models, LAM and SCM.

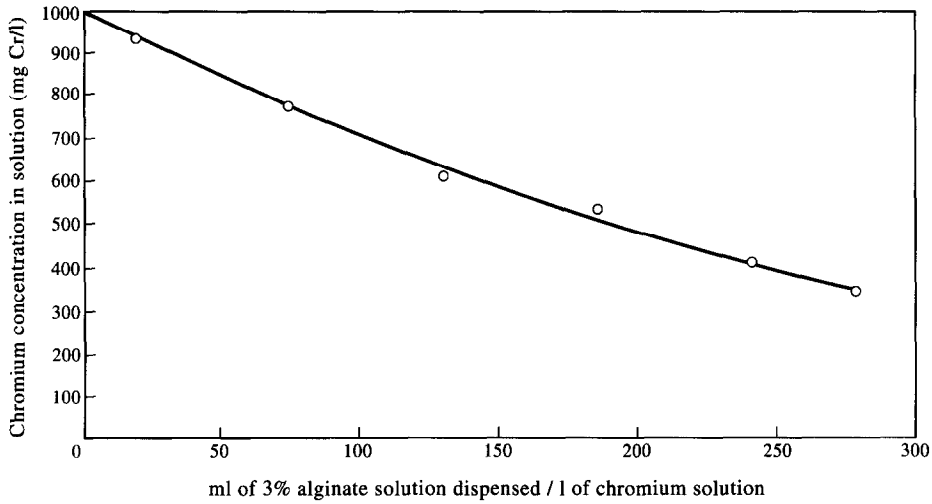

Fig. 11. Chromium concentration in solution as a function of the volume of a 3% alginate solution added to the chromium solution.

Using this process, for chromium concentrations between 400 and 1000 mg $Cr l^{-1}$, 0.08 g of chromium can be removed per gram of dry sodium alginate (2.3 mg $Cr ml^{-1}$ 3% algin solution). This procedure is similar to the one described by Jang *et al.* (1991) for copper, where a removal efficiency of the same order of magnitude—0.1 g $Cu g^{-1}$ dry alginate—was obtained.

Data indicate, that at high chromium concentration, it is more efficient to dispense sodium alginate directly in the chromium solution to remove chromium in excess of 400 mg $Cr l^{-1}$.

Figure 12 shows a possible example of a combination of this process with the process using preformed calcium alginate beads to remove chromium from an hypotetic effluent containing 1040 mg $Cr l^{-1}$ (20 mmol l^{-1}), reaching a low concentration value of 1.6 mg $Cr l^{-1}$. The system uses three stages, the first one removes the chromium above 400 mg $Cr l^{-1}$ by dropping the alginate solution directly. The second and third stages remove the remaining chromium with calcium alginate beads. Each step is performed in stirred tanks, and the chromium contaminated alginate beads are shrunk by air drying. As can be seen in Fig. 12, the overall chromium removal efficiency is 99.8%, and the volume reduction of contaminated effluent is 93.6%.

CONCLUSIONS

Analysing the results obtained in this work, the following conclusions about the removal of trivalent chromium by alginate can be made:

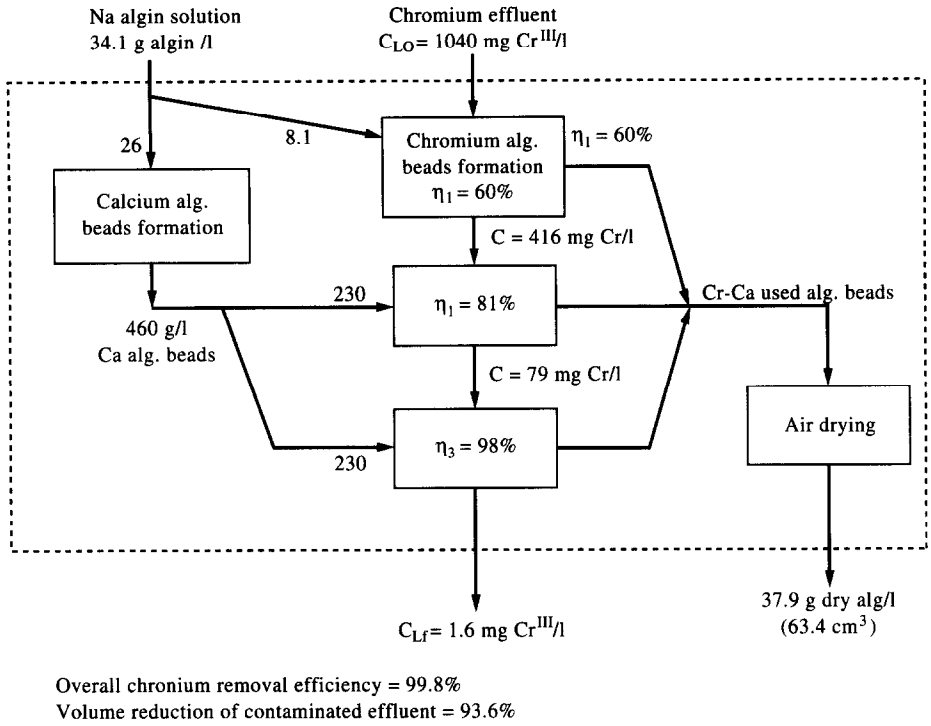

Fig. 12. Practical example of chromium removal from an effluent with initial concentration of 20 mmol/l, using three stages: in the first stage, the chromium concentration above 400 mg/l is removed by directly dispensing the sodium alginate solution; the second and third stages use calcium alginate beads.

The process is efficient and offers a practical possibility to remove trivalent chromium using calcium alginate beads.

Higher temperatures (in the range of 10 to 27°C) favour the sorption of chromium on calcium alginate beads, especially at chromium concentrations near the saturation of the beads.

At pH between 2 and 4, higher values increase chromium sorption.

The sorption isotherms are of type IV according to Brunauer classification, for they contain an inflexion point and finite values of sorption capacity.

There is more than one mechanism of chromium sorption by the alginate beads. Ionic exchange with calcium appears to be the dominant process in the range of lower chromium concentrations.

The rate equation $-dC_L/dt = kC_l^a$ describes reasonably well the kinetics of the sorption process (correlation coefficient superior to 0.995).

The Shrinking Core Model gave diffusion coefficients that were very dependent on chromium concentration, but mathematically adjusted better to the experimental results at low concentration than the Linear Absorption Model. This can be explained by the fact that at low concentrations, the ionic exchange is the governing mechanism.

The Linear Absorption Model mathematically adjusts better to the experimental results at higher chromium concentration than the Shrinking Core Model, which can be justified since in this region, the ionic exchange is no longer the main mechanism of sorption.

To remove trivalent chromium from concentrated solutions, better results can be obtained if, in a first step, the chromium above 400 mg $Cr\,l^{-1}$ is removed by directly dispensing the alginate solution on the chromium solution, to form chromium alginate beads, and then the remaining chromium is sorbed by calcium alginate beads.

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